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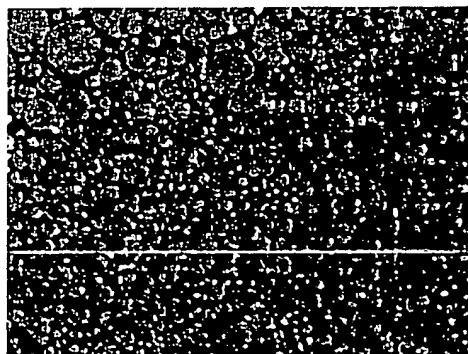
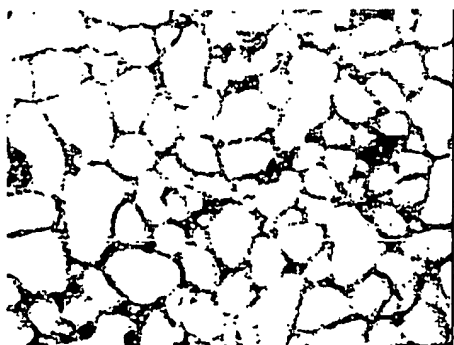
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(54) Title: **A METHOD FOR THE PRODUCTION OF CONDUCTIVE AND TRANSPARENT NANO-COATINGS AND NANO-INKS AND NANO-POWDER COATINGS AND INKS PRODUCED THEREBY**



(57) Abstract: The present invention provides for a cost-effective method for coating a substrate by conductive and/or transparent nano-powders in either ordered or random pattern, wherein said pattern is obtained either spontaneously or as a result of a printing technique. The present invention also provides for a conductive and transparent coating layer comprising metal nano-powders, and for conductive and transparent ink characterized by self-assembled network pattern, coating a substrata without altering significantly its transparency and/or conductivity characterizations.

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A METHOD FOR THE PRODUCTION OF CONDUCTIVE AND TRANSPARENT NANO-COATINGS AND NANO-INKS AND NANO-POWDER COATINGS AND INKS PRODUCED THEREBY

FIELD OF THE INVENTION

The present invention generally relates to a method for the production of transparent conductive coatings and inks and nano-powder coatings and inks obtained by this method.

BACKGROUND OF THE INVENTION

Nano particles, especially metal nano particles have very special properties which are directly related to their dimensions and to the fact that a large ratio of the atoms in the particle are in the surface of the particle or at particle and grain boundaries. These properties include optical properties, sintering and diffusion properties, electrical properties like capacitance, impedance and resistance, catalytic activity and many others.

These improved properties have a range of uses and applications; e.g. catalysts for chemical reactions, electrodes, fuel cells, medical devices, water cleaning technologies, electronic devices, coatings, and more.

U.S. Pat. 5,476,535 to the applicant present a method for the production of nano-powders, especially of silver. This process comprising the steps of (a) forming an aluminum-silver alloy of a specific blend composition; (b) leaching the aluminum ingredient by a series of consequent leaching steps wherein a fresh leaching agent is reacting the treated solid material, providing a gradually porous and homogeneous silver alloy. Ultrasonic oscillations are applied in step (c), disintegrating the agglomerate and enhancing the penetration of the leaching agent into the ever growing porous of the alloy by the application of a plurality of ultrasonic oscillations. The leaching agent is leaving silver agglomerate in step (d), and then the agglomerate is washed and dried in a final step.

According to U.S. Pat. No. 6,012,658 to the applicant et al., the very same process was used as is to form metal flakes. Thus, the following two main steps were introduced: comminuting

the alloys obtained by the aforementioned U.S. Pat. No. 5,476,535 into defined particles, and then filtering the obtained particles into strip-like highly porous alloys of predetermined characteristics.

SUMMARY OF THE INVENTION

It is the core of the present invention to provide useful and novel a method for coating a substrate by conductive and/or transparent nano-powders in either ordered or random pattern, wherein said pattern is obtained either spontaneously or as a result of a printing technique. It is well in the scope of the present invention to use of nano metal additive to produce a transparent-conductive coating such in the case of nano titanium dioxide additive that was proved useful for the production of coatings transparent to visible light and opaque to UV wave lengths; in the case of nano silica additive, that was found useful for the production of transparent coatings with special resistance performance; and in the case of nano pigments, that proved useful for the production of transparent colored coatings.

It is also an object of the present invention to provide a useful and novel method for the production of conductive and transparent coatings comprising metal nano-powders. Said method comprising the steps of (i) admixing metal nano powder in a solvent with at least one ingredient of the group: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; (ii) applying the homogenized mixture obtained above on a surface to be coated by various manners: screen printing, spreading, spin coating, dipping etc.; (iii) evaporating the solvent from said homogenized mixture; and (iv) sintering the coated layer so a conductive and transparent coating is obtained on top of said surface.

It is in the scope of the present invention wherein the metal nano powders are used alone or in combination with conductivity improving additive selected from at least one of the group: metal colloids and/or metal reducible salt and/or organic metal complexes and/or organo metal compounds which decompose to form conductive materials. Preferably, the concentration of the metal nano powder in the admixed solution is between 1% (wt) to 50% (wt) and more particularly, in the range of 2% (wt) to 10% (wt).

It is further in the scope of the present invention wherein the admixed solution comprising organic solvent or a mixture of organic solvents. Those organic solvents are characterized by an evaporation rate higher than the evaporation rate of water at ambient conditions. The concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 20% (wt) to 85% (wt). More specifically, their concentration in the narrow range 40% (wt) to 80% (wt). It is acknowledged in this respect that the solvents can be selected from at least one of the group of petroleum ether, hexanes, heptanes, toluene, benzene, dichloroethane, trichloroethylene, chloroform, dichloromethane, nitromethane, dibromomethane, cyclopentanone, cyclohexanone or any mixture thereof.

It is further in the scope of the present invention wherein the concentration of the aforementioned binder in the admixed solution is between 0% (wt) to 3% (wt). Preferably (but not limited to), the binder is selected from ethyl cellulose and/or modified urea.

It another object of the present invention to provide a useful and novel method for the production of ink or solution comprising metal nano-powders for the producing of transparent and conductive coatings. This method is in principle similar to the one defined above, and comprising the following steps: (i) admixing metal nano powder in a solvent with at least one ingredient of the group: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; (ii) admixing said homogenized mixture with water or water miscible solvent or mixture of water miscible solvents in the manner a W/O type emulsion is obtained (iii) applying the emulsion obtained above on said surface to be coated spreading, spin coating, dipping etc.; (iv) evaporating the solvent from said homogenized mixture in the manner that a self-assembled network-like pattern is developed *in situ*; and lastly, (v) sintering the network-like pattern so a conductive and transparent coating is obtained.

It is in the scope of the present invention wherein the concentration of the aforementioned surfactant or surfactants mixture is between 0% (wt) to 4% (wt) and/or wherein the concentration of the surfactant or surfactants mixture in the dispersed emulsion is between 0% (wt) to 4% (wt). Preferably, W/O emulsion is obtained by said methods. .

It is further in the scope of the present invention wherein the concentration of the water miscible solvent or mixture of water miscible solvents in the dispersed emulsion is between 5% (wt) to 70% (wt). Preferably (but not limited to), the surfactant or surfactants mixture defined above comprising at least one of the group of non ionic and ionic compounds, selected from SPAN-20, SPAN-80, glyceryl monooleate, sodium dodecyl sulfate, or any combination thereof. Moreover, it is also in the scope of the present invention wherein the concentration of the water miscible solvent or mixture of water miscible solvents in the dispersed emulsion is between 15% (wt) to 55% (wt).

It is further in the scope of the present invention wherein the aforementioned water miscible solvent or solvent mixture is selected from (but not limited to) at least one of the group of water, methanol, ethanol, ethylene glycol, glycerol, dimethylformamid, dimethylacetamid, acetonitrile, dimethylsulfoxide, N-methylpyrrolidone or any mixture thereof.

The present invention relates to a method as defined in any of the above, wherein the surface to be coated is selected from glass, either flexible or relatively non-flexible polymeric films or sheets or any combination thereof. More specifically, the present invention relates to the hereto-defined method, wherein the polymeric film comprising at least one of the group of polyesters, polyamides, polyimides, polycarbonates, polyethylene, polyethylene products, polypropylene, acrylate containing products, polymethyl metaacrylates (PMMA) their copolymers or any combination thereof and any other transparent substrate. Additionally or alternatively, the method defined above is comprises of another step of treating the surface to be coated by a means of corona treatment and/or coating by primer.

It is further in the scope of the present invention wherein the aforementioned primer is selected (but not limited to) from at least one of the group of 3-aminopropyl triethoxy silane, phenyl trimethoxysilane, glycidyl trimethoxysilane, commercially available Tween products, Tween-80, neoalkoxy tri(dioctylpropylphosphato) titanate or any combination thereof.

It is further in the scope of the present invention wherein the aforementioned nano-powder comprising metal or a mixture of metals selected from (but not limited to) silver, gold, platinum, palladium, nickel, cobalt, copper or any combination thereof.

It is further in the scope of the present invention wherein the spreading of the homogenized mixture on a surface to be coated is provided by a means selected from simple spreading; immersing; spin coating; dipping or any other suitable technique. Moreover, according to one embodiment of the present invention, the step of coating layer or layers provided by the spreading of the homogenized mixture on a surface to be coated is provided for a wet thickness of 5 to 200 microns.

It is further in the scope of the present invention wherein the sintering of the evaporated homogenized solution is provided in the temperature range of 50°C to 300°C for 0.5 to 2 hours. Alternatively, the sintering of the network-like pattern is provided in the temperature range of 50°C to 150°C for 2 to 30 minutes.

It another object of the present invention to provide a cost-effective and novel conductive and transparent coating layer comprising metal nano powders, produce in the method as defined in claim 1 or in any of its preceding claims. Additionally or alternatively, a conductive and transparent ink or coating layer or layers is provided by the present invention, and is characterized by self-assembled network pattern, produce in the method as defined in claim 11 or in any of its preceding claims.

It is thus also in the scope of the present invention wherein the aforementioned conductive and transparent coating layer is characterized by light transparencies in the range of 30% to 90% at 400 nm to 700 nm wavelength; resistances in the range of 0.1 Ω /square to 10 k Ω /square and by haze value in the range of 0.5% to 10%; and wherein the conductive and transparent ink layer is characterized by light transparencies in the range of 10% to 90% at 400 nm to 700 nm wavelength; resistances in the range of 0.1 Ω /square to 1,000 Ω /square, and by a haze value in the range of 0.1% to 5%.

It is further in the scope of the present invention wherein the conductive and transparent coating layer defined above is characterized by either ordered or random patterns, wherein said patterns are provided by printing, ink-jet printing, ink-jet disposition, self-assembling or self organizing or any other suitable technique. Said conductive and transparent coating layer or the multiple layer array may further characterized by that it provided a protective layer,

anti-scratch layer, a layer of an enhance conductivity, a layer of an enhance adhesion to a surface to be coated or any combination thereof. Moreover, the obtained conductive and transparent coating layer or the aforementioned multiple layer array may be especially adapted to be use in at least one of the group of screens, displays, electrodes, PCBs, ink-jet products, ink-jet disposition products, smart cards, RFID, antenna, thin-film transistors, LCDs or any combination thereof.

BRIEF DESCRIPTION OF THE FIGURES

In order to understand the invention and to see how it may be carried out in practice, preferred embodiments will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

- Figure 1 presenting a view taken by a means of a light microscope showing the self-assembling pattern of an ink disposed on a glass surface as obtained by the method of one embodiment of the present invention;
- Figure 2 presenting a view taken by a means of a light microscope showing the self-assembling pattern of an ink disposed on a glass surface as obtained by the method of another embodiment of the present invention;
- Figure 3 presenting a view taken by a means of a light microscope showing the self-assembling pattern of an ink disposed on a glass surface as obtained by the method of another embodiment of the present invention;
- Figure 4 presenting a view taken by a means of a light microscope showing the self-assembling pattern of an ink disposed on a glass surface as obtained by the method of another embodiment of the present invention; and
- Figure 5 presenting a view taken by a means of a light microscope showing the self-assembling pattern of an ink disposed on a polymeric film as obtained by the method of yet another embodiment of the present invention; and,
- Figure 6 presenting a view showing the printed pattern of ink disposed on a glass surface obtained by the method of another embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The following description is provided, along all chapters of the present invention, so as to enable any person skilled in the art to make use of said invention and sets forth the best modes contemplated by the inventor of carrying out this invention. Various modifications, however, will remain apparent to those skilled in the art, since the generic principles of the present invention have been defined specifically for a method for the production of metal nano powders coatings and inks and for all products produced thereby.

A novel method for the production of conductive and transparent coatings and inks comprising metal nano-powders (i.e., coatings or inks) is hereby presented. The hereto defined method takes full advantage of the fact that nano sized particles and grains have much larger surface areas than bulk materials, have special optical properties and can be worked to produce a conductive phase. It is according to the present invention that by coating a substrate with an "ink", solution or paste that was previously dispersed, cost-effective nano conductive materials and/or conductive transparent coating are produced. Those coatings and inks are generally characterized by (1) light transparencies between 40% to 90% in the visible range of about 400nm to 700nm wavelength; by (2), resistances between $0.1 \text{ } \Omega/\text{square}$ to $9 \text{ k}\Omega/\text{square}$, and (3), by a relatively low haze values, generally ranges from 1% to 10%.

The term 'coating' is referring according to the present invention to any conductive and transparent optical layer produced in the manner of admixing metal nano powder in a solvent with at least one ingredient of the group: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; spreading the homogenized mixture obtained above on a surface to be coated; evaporating the solvent from said homogenized mixture; and than sintering the coated layer so a conductive and transparent coating is obtained on top of said surface.

The term 'ink' is referring according to the present invention to any ink containing nano-powders of metal or metals, especially emulsion based compositions provided for coloring materials, or alternatively, to legend ink (marking ink) suitable for printing on printed circuit boards (PCB's).

More specifically, the term 'ink' is referring according to the present invention to any conductive and transparent topical pattern produced in the manner of admixing metal nano powder in a solvent with at least one ingredient of the group: binder, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained; admixing said homogenized mixture with water or water miscible solvent or mixture of water miscible solvents in the manner a W/O type emulsion is obtained; spreading the homogenized mixture obtained above on said surface to be coated; evaporating the solvent from said homogenized mixture in the manner that a self-assembled network-like pattern is developed *in situ*; and then sintering the network-like pattern so a conductive and transparent ink is obtained.

The inks (e.g., ink paste, inks, solutions, coatings) according to the present invention are especially adapted for use in or on top of transparent substrates. The aforementioned ink is adapted for coating, covering, immersing, dipping, and/or entrapping on top or into either solid or semi-solid matrix, or by means of any other suitable technique on such as glass or any polymer matrix, including flexible, semi-flexible or rigid materials. Due to their significant transparency in the visible wavelength range of about 400nm to 700nm, the aforementioned conductive ink is especially useful for screens, displays, liquid crystalline displays, smart cards and/or for any technology using ink-jets printers or any other technology of printing electronic matter.

The coating techniques that we have used are screen-printing, manual applicator and manual spreading. Other suitable techniques such as spin coating, spray coating, ink jet printing, offset printing and any suitable technique can also be used. Any type of transparent and non-transparent substrate can be coated for example glass, polycarbonate, polymer films and others.

Various ink/paste and coating systems have been found useful to produce a transparent-conductive coating, which differ in the formulation concept, and main ingredients leading to the conductivity and transparency. The main ingredients are selected from metal nano powder; metal nano powder with metal colloids; metal nano powder with a metal reducible salt; and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials and all the above in a self-organizing system.

These nano metal based coating systems achieve light transmittances of up to 95% (measured between 400 nm and 700 nm), low haze values, with resistances as low as $1 \text{ } \Omega/\text{square}$.

The ink or pastes are prepared according to the general procedure described bellow. Care has to be taken to achieve a good dispersion of the conductive additives (metal nano powders, salts, colloids and other additives).

The substrate is coated with the ink or paste. The coating can be performed in the different techniques previously described. The technique is chosen to enable control of physical parameters such as thickness and printed geometries (to obtain the desired transmittance and resistance). Sample may be heated, to obtain the desired resistance, to between 50°C to 300°C for 0.5 to 2 hours.

The term 'sintering' is referring according to the present invention to any process of forming objects from a metal powder by heating the powder at a temperature below its melting point. In the production of small metal objects it is often not practical to cast them. Through chemical or mechanical procedures a fine powder of the metal can be produced. When the powder is compacted into the desired shape and heated, i.e., sintered, for up to three hours, the particles composing the powder join together to form a single solid object.

EXAMPLES

Examples for formulations for each method are described bellow. These are only representative examples and are described hereby to demonstrate the wide range of possibilities this invention covers, by which we can use the special properties of nano metal powders. It is further acknowledged that the formulations of the hereto-described examples may similarly be made with different binders, solvents, metal powders, additives, polymers, buffers, surfactants, dispersants and/or coupling agents. Nevertheless, according to the present invention, nano powder metals and/or nano powder metal salts characterized by small particle size ($D_{90} < 0.1 \text{ } \mu\text{m}$) which are conductive are especially preferred. Concentrations can be adjusted to control the viscosity and the resistance and transparency of the coated substrate.

Example 1

Admixing a binder, e.g., ethyl cellulose, 13% by weight, in a solvent, e.g., aromatic esters and aldehydes, preferably terpinol. Further homogenizing 25 parts by weight of the obtained binder solution by a means of a high rpm homogenizer the following materials: Silver nano-powder ($D_{90} < 0.1 \mu\text{m}$), 50% (w/w), a solvent such as terpinol 20% (w/w) and a coupling agent, e.g., isopropyl dioleic(dioctylphosphato)titanate, also known as the commercially available NDZ-101 KRTTS, 1% (w/w).

Example 2

Admixing metals nano powder, e.g., colloidal silver, 12% (w/w), a binder which is an adhesion promoter, such as Polyvinyl Pyrrolidone (PVP), 2.5% (w/w), and water, 32% (w/w). All components are intensively mixed by a means of an ultrasonic energy and/or high rpm dispersing equipment. Separately, Admixing metals nano powder, e.g., silver nano powder ($D_{90} < 0.1 \mu\text{m}$), 14% (w/w), solvent, such as ethanol, 39.5% (w/w), by a means of a high rpm homogenizer. Finally, admixing solution obtained in first step with the solution obtained in the second step, so a homogenized solution is obtained.

Example 3

Admixing metals nano powder, e.g., silver formate salt -1 parts by weight, a dispersant, e.g., trioctylphosphine oxide (TOPO), 2% (w/w) in a solvent, e.g., ethyl Acetate, 80% (w/w). Heating the solution to about 60°C until all components dissolve. Admixing metals nano powder, e.g., silver powder ($D_{90} < 0.1 \mu\text{m}$), 17% (w/w) into the brown solution obtained in the first step, and subsequently homogenizing the obtained mixture by a means of a high rpm homogenizer.

Example 4

Admixing metals nano powder, e.g., dissolve silver nitrate, 4% (w/w) in a buffer, e.g., ammonia, 25% solution, 9.5% (w/w). Further admixing water, 47% (w/w) and a dispersant, such as poly-carboxylic ammonium salt (e.g., the commercially available T1124 product), 3.5% (w/w), solvent, e.g., ethanol, 24% (w/w) and metals nano powder, e.g., silver powder ($D_{90} < 0.1 \mu\text{m}$), 12% (w/w) and subsequently homogenizing the obtained mixture by a means of a high rpm homogenizer.

The optical and resistance data for metal nano powders coatings and inks produced in the hereto-defined examples are hereto provided:

Table 1: Optical and resistance data for nano metal powders coatings and inks

Example No.	Printing Geometry	Transmittance %	Resistance ? / square	Haze %	Remarks
Blank		92		8	Glass slides
1	Screen	60-90	4- 100	0.5-2	UV opacity
2	Continuous	20-85	2-4000	1-10	UV opacity
3	Continuous	30-90	10-1200	1-10	UV opacity
4	Continuous	55-90	150-8000	1-6	UV opacity

Light transmittance measured between 400nm and 700nm. Heat treatment was provided at 280°C for about one hour.

It is hence according to another embodiment of the present invention, to present a new and simple method of producing transparent and conductive coating and inks on top or in glass and/or polymeric surfaces. This novel method is based on spreading of a predetermined mixture defined above on the surface to be coated. While an organic solvent is evaporated from the spread mixture, the self-assembled network-like pattern is developed *in situ*, i.e., on the surface. After drying is completed, the developed pattern is sintered at relatively low temperatures, e.g. at a temperature ranges from 50°C to 150°C for about 2 to 30 minutes. The final resistance of conductive layer lies in the range of about 1 to 1,000 Ohm/square, light transmittance is in the range of about 50 to 95%, and the haze value is in the range of about 0.5 to 5%.

The said special mixture is a *W/O* type emulsion of water or water miscible solvent (or a mixture of these solvents) in a suspension of metal fine particles in an organic solvent or mixture of two or more solvents not miscible with water.

It is according to this embodiment of the present invention, wherein the mixture also contains at least one emulsifying agent, binder or any mixture thereof. Hence, the dispersed phase is selected, according to yet another embodiment of the present invention from the group comprising yet not limited to water, methanol, ethanol, ethylene glycol, glycerol, dimethyl formamid, dimethyl acetamid, acetonitrile, dimethyl sulfoxide, N-methyl pyrrolidone and/or other water miscible solvents.

According to yet another embodiment of the present invention, the continuous phase is selected from the group comprising yet not limited to petroleum ether, hexanes, heptanes, toluene, benzene, dichloroethane, trichloroethylene, chloroform, dichloromethane, nitromethane, dibromomethane, cyclopentanone, cyclohexanone or any mixture thereof. Preferably, the solvent or solvents used in this continuous phase are characterized by higher volatility than that of the dispersed phase.

Similarly, the emulsifying agents are selected from the group comprising yet not limited to non ionic and ionic compounds, such as the commercially available SPAN-20, SPAN-80, glyceryl monooleate, sodium dodecylsulfate, or any combination thereof. Moreover, the binders are selected, yet not limited to modified cellulose, such as ethyl cellulose MW 100,000-200,000, modified urea, e.g., the commercial available BYK-410, BYK-411, BYK-420 produced by BYK-Chemie Ltd.

It is according to yet another embodiment of the present invention, wherein the metal fine particles and nano-powders are selected, yet not limited to silver, gold, platinum, palladium, nickel, cobalt, copper or any combination thereof, wherein said metal or mixture of metals is characterized by an average particle size smaller than 1 micron, better smaller than 0.5 and most preferably smaller than 0.1 micron. The small particle size provides the improved optical properties of the coatings obtained in the method provided by the present invention. According to one specifically preferred embodiment of the present invention, the aforementioned metal or mixture of metals is selected from precious metals due to their enhanced chemical stability and improved electrical conductivity.

Table 2. Basic mixture formulation of the nano-inks and nano-powders obtained by the method as defined and described in the above mentioned examples.

Component	Min. content, %	Max. content, %
Organic solvent or mixture	40	80
Binder	0	3
Emulsifying agent	0	4
Metal powder	2	10
Water miscible solvent or mixture	15	55

The mixture should be prepared by the following way: Emulsifying agent and/or binder dissolved in organic solvent or mixture and metal powder added. Metal powder should be dispersed in organic phase by ultrasonic treatment, high shear mixing, high speed mixing or any other way used for preparation of suspensions and emulsions. After this water miscible solvent or mixture added and W/O type emulsion prepared by ultrasonic treatment, high shear mixing, high speed mixing or any other way used for preparation emulsions.

The mentioned above self-assembled network pattern can be developed on different surfaces: glass, polymeric films and sheets (polyesters, polyamides, polycarbonates, polyethylene, polypropylene etc.). The surface to be coated may be both untreated and treated for surface properties changing (corona treatment or coating by primer). As primers may be used 1-2% acetone or hexane solutions of 3-Aminopropyl Triethoxy silane, Phenyl Trimethoxysilane, Glycidyl Trimethoxysilane, Tween-80, Neoalkoxy Tri(dioctylpropylphosphato) titanate etc.). Coating techniques may be following simple spreading, spin coating, dipping). Wet thickness of coating – from 5 to 200 microns.

Additional technique of polymeric films coating is a developing of self-assembled network on glass and printing of the pattern on polymer.

Example 5

Admixing a surfactant such as SDS, 0.1g in 40 g of water. Admixing than a binder, e.g., ethyl cellulose, 1g, in a solvent, e.g., in toluene, 60g and nano powder metals, e.g., silver nano-powder ($D_{90} < 0.1 \mu\text{m}$), 8g. Than, homogenizing the obtained solution by a means of ultrasonic energy and/or high rpm dispersing equipment. Lastly, admixing 31 g of the solution obtained by the first step with the solution obtained by the second step.

Example 6

Admixing a metals nano powder, e.g., silver powder (maximal particle size is lower 0.12 micron), 4 g; a solvent, e.g., 1,2-Dichloroethane, 30 g; a binder, e.g., BYK-410, 0.2 g; and homogenizing the solution by a means of an ultra sound at 180W power for 1.5 min. admixing distilled water, 15g and homogenizing the obtained emulsion by an ultra sound means at 180W power for 30 sec. This formulation was printed on glass surface and provided good developed network with big cells (above 40 μ up to 70 μ and lines about 2-6 μ width). Resistance was in the range of 7 to 40 Ω /square, transparency from 72 to 81%, and haze value between 0.8 to 1.8%. Reference is made now to Fig. 1, presenting a view taken by a means of a light microscope showing the pattern on glass surface as obtained by the method as described in example 6.

Example 7

Admixing metals nano powder, e.g., silver powder (maximal particle size is lower 0.12 micron), 4 g; a solvent, e.g., toluene, 30 g, a binder, e.g., BYK-410, 0.2 g homogenizing the solution by a means of an ultra sound at 180W power for 1.5 min. admixing distilled water, 15g and homogenizing the obtained emulsion by an ultra sound means at 180W power for 30 sec. This formulation printed on glass surface gives good developed network with small cells (about 10 μ and lines about 1 to 4 μ width). Resistance was in the range of 7 to 40 Ω /square, transparency was between 45 to 65%, and haze value between 1.5 to 3.0% after sintering at 150°C for 5 min. Reference is made now to Fig. 2, presenting a view taken by a means of a light microscope showing the pattern on glass surface as obtained by the method as described in example 7.

Example 8

Admixing a binder, e.g., BYK-410, 0.06 g; a surfactant, e.g., SPAN-80, 0.03g; a solvent, e.g., cyclopentanone, 0.8g and toluene, 16g; nano powder metals, e.g., silver powder (maximal particle size is lower 0.12 micron), 0.8g and homogenizing the obtained solution by an ultra sound means at 180W power for 30 seconds. Admixing distilled water, 9ml and homogenizing the obtained emulsion by an ultra sound means at 180W power for 20sec. This formulation was printed on glass pretreated with 1% acetone solution of 3-aminopropyl

triethoxy silane and gave good developed network with cells of 40μ to 70μ and lines about 2 to 6μ width. Resistance was between 2 to $16\ \Omega/\text{square}$, transparency was between 72 to 81%, haze value was between 0.8 to 1.8% after sintering at 50°C for 30 min in formic acid vapor. The pattern printed from glass to different polymeric films almost doesn't change electrical and optical properties.

Example 9

Admixing metals nano powder, e.g., silver powder (maximal particle size is lower 0.12 micron), 4g; a solvent, e.g., trichloroethylene, 30g; a binder, e.g., BYK-410, 0.2g; and homogenizing the obtained solution by an ultra sound means at 180W power for 1.5 min. Admixing distilled water, 15ml and homogenizing the obtained emulsion by an ultra sound means at 180W power for 30 sec. This formulation was printed on glass surface and gave good developed network with small cells: about 10 to 40μ and lines of about 2 to 4μ width). Resistance was between 7 to $40\ \Omega/\text{square}$, and transparency was 45 to 65% after sintering at 150°C for 5 min. This formulation provided useful also in the case when high-speed stirrer (Premier-type) is used instead of the ultra sound sonication. In this case, the obtained network cells are bigger and the transparency is improved. This formulation also has better performance while printed on polymer films not dissolved by trichloroethylene, such as PET, PEN, polyethylene. Reference is made now to Fig. 3, presenting a view taken by a means of a light microscope showing the pattern on glass surface as obtained by the method as described in example 9.

Example 10

Admixing a binder, e.g., BYK-410, 0.06g; a surfactant, e.g., SPAN-20, 0.03g, a solvent mixture, such as cyclohexanone, 0.8g and trichloroethylene, 24g; metals nano powder, e.g., silver powder (maximal particle size is lower 0.12 micron), 1g and homogenizing the obtained solution by an ultra sound means at 180W power for 30 sec. Admixing distilled water, 9ml and homogenizing the obtained emulsion by an ultra sound means at 180W power for 20 sec. This formulation was printed on glass pretreated with 1% acetone solution of 3-aminopropyl triethoxy silane and gave good developed network with cells of 50μ up to 100μ , and lines about 2 to 8μ width. Resistance was $1.8\text{-}10\ \Omega/\text{square}$, transparency 79-86%,

haze value 1.8 to 2.8% after sintering at 50°C for 30 min in formic acid vapor. Reference is made now to Fig. 4, presenting a view taken by a means of a light microscope showing the pattern on glass surface as obtained by the method as described in example 10. The pattern printed on various polymeric films and did not change electrical and optical properties significantly. Reference is made now to Fig. 5, presenting a view taken by a means of a light microscope showing the pattern on polymeric film as obtained by the method as described in example 10.

Example 11

Admixing a binder, e.g., BYK-411, 0.06 g; a surfactant, e.g., SPAN-80, 0.2 g; a solvent mixture, e.g., cyclohexanone, 1 g and petroleum ether, 10 g; metals nano powder, e.g., silver powder (maximal particle size is lower 0.12 micron), 1g and homogenizing the obtained solution by an ultra sound means at 180W power for 30 sec. Admixing distilled water, 7ml and homogenizing the obtained emulsion by an ultra sound means at 180W power for 20 sec. This formulation was printed on polyimide polymer pretreated with 1% acetone solution of phenyl trimethoxysilane and gave a good developed network characterized by cells of above 20 μ up to 60 μ , and lines about 2 to 6 μ width. The resistance was between 20 to 30 Ω /square, transparency 68 to 78%, and the haze value was between 8 to 10% after sintering at 150°C for 5 min.

CLAIMS

1. A method for coating a substrate by conductive and/or transparent nano-powders in either ordered or random pattern, wherein said pattern is obtained either spontaneously or as a result of a printing technique.
2. The method according to claim 1, useful for the production of conductive and transparent coatings comprising metal nano-powders, said method comprising:
 - a. admixing metal nano powder in a solvent with at least one ingredient of the group selected from: binder, surfactant, additive, polymer, buffer, dispersant and/or coupling agent in the manner a homogenized solution is obtained;
 - b. applying the homogenized mixture obtained above on a surface to be coated;
 - c. evaporating the solvent from said homogenized mixture; and,
 - d. sintering the coated layer providing a conductive and transparent coating on top of said surface.
3. The method according to claim 2, wherein the metal nano powder is selected from at least one of the group: metal nano powder; metal nano powder with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials.
4. The method according to claim 3, wherein the concentration of the metal nano powder in the admixed solution is between 1% (wt) to 50% (wt).
5. The method according to claim 3, wherein the concentration of the metal nano powder in the admixed solution is between 2% (wt) to 10% (wt).
6. The method according to claim 2, wherein the admixed solution comprising organic solvent or a mixture of organic solvents, characterized by an evaporation rate lower than the evaporation rate of water.
7. The method according to claim 2, wherein the concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 20% (wt) to 85% (wt).

8. The method according to claim 2, wherein the concentration of the organic solvent or the mixture of organic solvents in the admixed solution is between 40% (wt) to 80% (wt).
9. The method according to claim 2, wherein the solvent is selected from at least one of the group of petroleum ether, hexane, heptanes, toluene, benzene, dichloroethane, trichloroethylene, chloroform, dichloromethane, nitromethane, dibromomethane, cyclopentanone, cyclohexanone or any mixture thereof
10. The method according to claim 2, wherein the concentration of the binder in the admixed solution is between 0% (wt) to 3% (wt).
11. The method according to claim 2, wherein the binder is selected from ethyl cellulose and/or modified urea.
12. The method according to claim 1, useful for the production of conductive and transparent ink comprising metal nano-powders, said method comprising;
 - a. admixing metal nano powder in a solvent with at least one ingredient of the group selected from: binder, additive, polymer, buffer, oxidizing agent, dispersant and/or coupling agent in the manner a homogenized solution is obtained;
 - b. dispersing a surfactant solution in a water miscible solvent or mixture of water miscible solvents so an emulsion is obtained;
 - c. admixing said homogenized mixture in said emulsion;
 - d. spreading the homogenized mixture obtained above on said surface to be coated;
 - e. evaporating the solvent from said homogenized mixture in the manner that a self-assembled network-like pattern is developed *in situ*; and,
 - f. sintering the network-like pattern providing a conductive and transparent ink.
13. The method according to claims 2 or 12, wherein the concentration of the surfactant or surfactants mixture is between 0% (wt) to 4% (wt).
14. The method according to claim 12, wherein the concentration of the surfactant or surfactants mixture in the dispersed emulsion is between 0% (wt) to 4% (wt)

15. The method according to claim 12, wherein a W/O emulsion is obtained.
16. The method according to claim 12, wherein the concentration of the water miscible solvent or mixture of water miscible solvents in the dispersed emulsion is between 5% (wt) to 70% (wt).
17. The method according to claim 12, wherein the surfactant or surfactants mixture comprising at least one of the group of non ionic and ionic compounds, selected from SPAN-20, SPAN-80, glyceryl monooleate, sodium dodecyl sulfate, or any combination thereof.
18. The method according to claim 12, wherein the concentration of the water miscible solvent or mixture of water miscible solvents in the dispersed emulsion is between 15% (wt) to 55% (wt).
19. The method according to claim 12, wherein the water miscible solvent is selected from at least one of the group of water, methanol, ethanol, ethylene glycol, glycerol, dimethylformamid, dimethylacetamid, acetonitrile, dimethylsulfoxide, N-methylpyrrolidone or any mixture thereof.
20. The method according to claim 1, wherein the surface to be coated is selected from glass, either flexible or relatively non-flexible polymeric films or sheets, polyethylene products, polypropylene, acrylate containing products, PMMA, their co-polymers or any combination thereof.
21. The method according to claim 20, wherein the polymeric film comprising at least one of the group of polyesters, polyamides, polycarbonates, polyethylene, polypropylene, their copolymers or any combination thereof.
22. The method according to claim 2, additionally comprising the step of treating the surface to be coated by a means of corona treatment and/or coating by primer.

23. The method according to claim 22, wherein the primer is selected from at least one of the group of 3-aminopropyl triethoxy silane, phenyl trimethoxysilane, glycidyl trimethoxysilane, commercially available Tween products, Tween-80, neoalkoxy tri(dioctylpropylphosphato) titanate or any combination thereof.
24. The method according to claim 1 wherein the nano-powder comprising metal or a mixture of metals selected from silver, gold, platinum, palladium, nickel, cobalt, copper or any combination thereof.
25. The method according to claim 2 wherein polymer to be admixed in the homogenized solution are water miscible polymers.
26. The method according to claim 1 wherein the nano-powder comprising metal is admixed with metal colloids; metal nano powder with a metal reducible salt and/or organic metal complexes and/or organo-metal compounds which decompose to form conductive materials
27. The method according to claim 2, comprising the step of polymerizing a monomer in the presence of catalyst and/or oxidizing agent and/or reducing agent, in the manner a water miscible polymer is obtained in the homogenized solution.
28. The method according to claim 2, wherein the spreading of the homogenized mixture on a surface to be coated is provided by a means selected from simple spreading; bar spreading, immersing; spin coating; doping and/or dipping.
29. The method according to claim 28, wherein the coating layer or layers provided by the spreading of the homogenized mixture on a surface to be coated is characterized by a wet thickness of 5 to 200 microns.
30. The method according to claim 2, wherein the sintering of the evaporated homogenized solution is provided in the temperature range of 50°C to 300°C for 0.5 to 2 hours.

31. The method according to claim 12, wherein the sintering of the network-like pattern is provided in the temperature range of 50°C to 150°C for 2 to 30 minutes.
32. A conductive and transparent coating layer comprising metal nano powders, produced in the method as defined in claim 1.
33. A conductive and transparent coating layer comprising metal nano powders, produced in the method as defined in claim 2.
34. A conductive and transparent ink characterized by self-assembled network pattern, produce in the method as defined in claim 12.
35. The conductive and transparent coating according to claims 32 or 33, characterized by light transparencies in the range of 30% to 95% at 400 nm to 700 nm wavelength; resistances in the range of 0.1 Ω /square to 20 k Ω /square and by haze value in the range of 0.5% to 10%.
36. The conductive and transparent ink according to claim 34, characterized by light transparencies in the range of 10% to 90% at 400 nm to 700 nm wavelength;; resistances in the range of 0.1 Ω /square to 1,000 Ω /square, and by a haze value in the range of 0.1% to 5%.
37. The conductive and transparent coating layer according to claims 32-34, characterized by either ordered or random patterns, wherein said patterns are provided by printing, ink-jet printing, ink-jet disposition, self-assembling or self organizing.
38. The conductive and transparent coating layer or a multiple layer array according to claim 37, further characterized by that it provided a protective layer, anti-scratch layer, a layer of an enhance conductivity , a layer of an enhance adhesion to a surface to be coated or any combination thereof.
39. The conductive and transparent coating layer or a multiple layer array according to claim 37, adapted to be use in at least one of the group of screens, displays, electrodes, PCBs,

ink-jet products, ink-jet disposition products smart cards, RFID, antenna, thin-film transistors, LCDs or any combination thereof.

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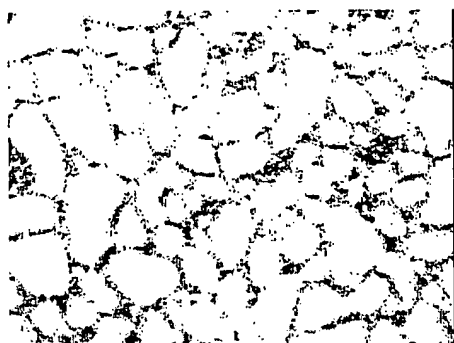


Fig. 1

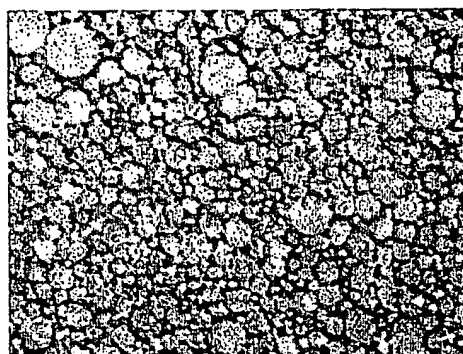


Fig. 2

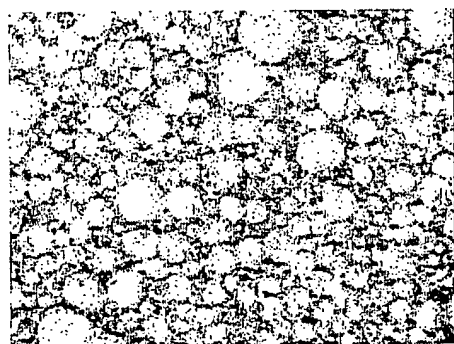


Fig. 3

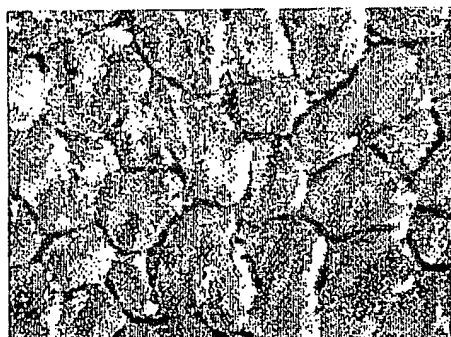


Fig. 4

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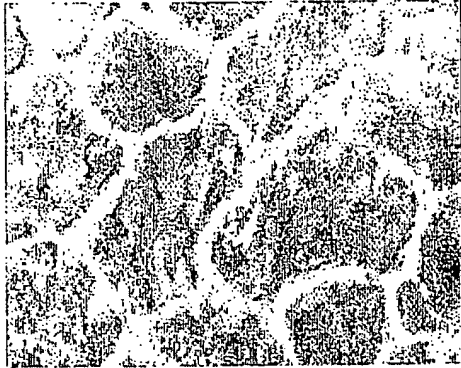


Fig. 5

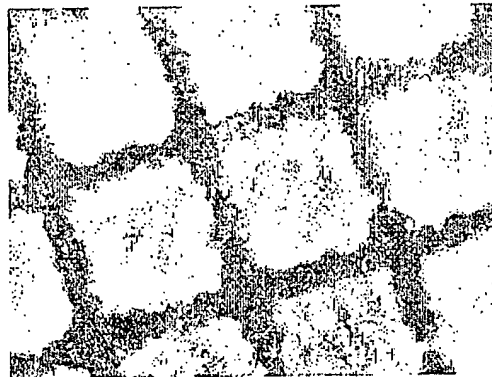


Fig. 6

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IL 03/00502

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 03 038002 A (BASSA AMAL;YISSUM RES DEV CO ; ABO MOKH RIAM (IL); MAGDASSI SHLOMO) 8 May 2003 (2003-05-08) page 10, line 16; claims; examples ---	1-5,10, 13,14, 24-39
E	EP 1 323 793 A (KOREA INST SCIENCE TECHNOLOGY ;SAMSUNG ELECTRONICS CO LTD (KR)) 2 July 2003 (2003-07-02) column 6, line 7-11; claims ---	1-38
X	US 5 922 403 A (TECLE BERHAN) 13 July 1999 (1999-07-13) column 4, line 18-50 -column 7, line 12	1,20,26, 32,35-38
Y	column 11, line 58 --- -/--	1-38

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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International Application No

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